Supporting Information

Alkynylation/Dearomatizative Cyclization to Construct

Spiro[5.5]undecanes

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**General Information**

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on GF254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petro ether was 60-90°C. CH₂Cl₂ was dried by distillation over CaH₂. Benzene and THF was dried by distillation over Na/K alloy. CH₃NO₂ was distilled over anhydrous CaCl₂ and further dried over 4Å molecular sieve. Commercially available reagents and solvents were used without any purification. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solution on Bruker AX-400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker Apex II by means of the ESI technique.

**Experimental Procedures and Analytical Data**

**Preparation of 5a.** Cu(OTf)₂ (21.2mg, 0.0588mmol) was added in dry CH₂Cl₂ (2.0ml) under Ar atmosphere. Then, ZnMe₂ in toluene (1.2M, 3.06ml) was added. After 10min, 2a (245μL, 2.94mmol) was added. 2 h later, the solution was cooled to 0 °C and treated with compound 1a (112mg, 0.735mmol) dissolved in CH₂Cl₂ (2.0ml). The resulting mixture was stirred at room temperature for 12h. After the reaction was completed (monitoring with TLC), it was quenched with saturated aqueous NH₄Cl solution. The mixture was extracted with EtOAc (3×20 mL). The organic layers were washed with brine, dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by flash column chromatography to afford compound 5a as a light yellow liquid (147mg, 90% yield).

2-(1-hydroxy-4-methoxybut-2-yn-1-yl)-4-methoxyphenol (5a). ¹H NMR (400 MHz, CDCl₃) δ 7.03 (s, 1H), 6.91 (d, 1H, J = 2.8Hz), 6.75-6.82 (m, 2H), 5.67 (s, 1H), 4.18 (d, 2H, J = 1.2Hz), 3.75 (s, 3H), 3.39 (s, 3H).

**General procedure.** Cu(OTf)₂ (21.2mg, 0.0588mmol) was added in dry CH₂Cl₂ (2.0ml) under Ar atmosphere. Then, ZnMe₂ in toluene (1.2M, 3.06ml) was added. After 10min, terminal alkyne (2.94mmol) was added. 2 h later, the solution was cooled to 0 °C and treated with substituted
salicylaldehyde (0.735mmol) dissolved in CH₂Cl₂ (2.0ml). The resulting mixture was stirred at room temperature for 12h. After salicylaldehyde was disappeared (monitoring with TLC), the solution was opened to atmosphere, 4 Å molecular sieve and functionalized 1, 3-butadiene (3.675mmol) was added. 5min later, dropped HCO₂H (1.10mmol). The mixture was stirred 12h at room temperature and filtered through short diatomite columns to afford crude product. Further purification by flash column chromatography afforded product.

**3-methoxy-2'-[(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a' -hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4a).**

The title compound was obtained in 46% yield as a light yellow solid. m.p. 102-104°C. ¹H NMR (400 MHz, CDCl₃) δ 6.84 (dd, 1H, J=3.2Hz, J=10.0Hz), 6.09 (d, 1H, J=10.0Hz), 5.51-5.52 (m, 1H), 5.15 (d, 1H, J=3.2Hz), 3.94 (t, 2H, J=1.8Hz), 3.66 (s, 3H), 3.23 (s, 3H), 2.85-2.89 (m, 2H), 2.27-2.32 (m, 2H), 1.46-1.55 (m, 1H), 1.37-1.43 (m, 3H), 1.14-1.22 (m, 2H), 1.11 (s, 3H), 1.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 205.9, 152.4, 145.3, 141.4, 127.6, 114.3, 104.7, 86.2, 76.8, 59.7, 56.9, 55.0, 44.2, 40.2, 37.1, 36.1, 29.9, 29.4, 28.8, 28.6, 21.1. IR[νmax cm⁻¹] 3263, 3051, 2924, 2849, 2666, 2367, 2222, 1993, 1871, 1783, 1718, 1670, 1638, 1587, 1461, 1408, 1363, 1237, 1188, 1096, 1040, 1004, 906, 829, 773, 738, 691, 605, 539, 489, 455. MS-ESI: m/z = 358 [M+NH₄]⁺. HRMS-ESI (m/z): [M+Na]+ calcd 363.1931; found 363.1936.

**2'-[(3-methoxyprop-1-yn-1-yl)-3,5',5'-trimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4b).**

The title compound was obtained in 36% yield as a light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.86 (dd, 1H, J=2.2Hz, J=9.8Hz), 6.05-6.08 (m, 2H), 5.51-5.53 (m, 1H), 3.94 (dd, 2H, J=2.0Hz, J=3.2Hz), 3.24 (s, 3H), 2.84-2.90 (m, 2H), 2.27-2.31 (m, 2H), 2.01 (d, 3H, J=1.2Hz), 1.36-1.52 (m, 5H), 1.16-1.24 (m, 1H), 1.11 (s, 3H), 1.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 206.5, 145.4, 145.2, 135.6, 131.5, 126.4, 114.4, 86.3, 77.2, 59.8, 56.9, 56.7, 44.2, 40.2, 36.6, 36.1, 29.9, 29.5, 28.8, 28.5, 21.5, 21.2. IR[νmax cm⁻¹] 3274, 3050, 2925, 2866, 2821, 2372, 2230, 1990, 1871, 1719, 1670, 1640, 1570, 1450, 1408, 1381, 1357, 1258, 1231, 1188, 1137, 1097, 1042, 1004, 947, 906, 824, 767, 737, 703, 643, 600, 507, 490, 437. MS-ESI: m/z = 342 [M+NH₄]⁺. HRMS-ESI (m/z): [M+Na]+ calcd 347.1982; found 347.1987.

**2'-[(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4c).**
The title compound was obtained in 20% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.99-7.03 (m, 1H), 6.41-6.48 (m, 2H), 6.10 (d, 1H, $J$=9.6Hz), 5.52-5.54 (m, 1H), 3.94 (t, 2H, $J$=1.6Hz), 3.25 (s, 3H), 2.89-2.96 (m, 2H), 2.27-2.34 (m, 2H), 1.37-1.49 (m, 4H), 1.15-1.25 (m, 2H), 1.10 (s, 3H), 1.05 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 206.4, 145.1, 141.8, 141.1, 126.8, 124.2, 114.5, 85.9, 76.9, 59.8, 57.8, 57.2, 44.1, 40.2, 36.6, 36.2, 30.0, 29.6, 28.8, 28.5, 21.2. IR[$\nu_{\text{max}}$ cm$^{-1}$] 3381, 3045, 2925, 2853, 2726, 2376, 2235, 1718, 1660, 1631, 1608, 1562, 1508, 1460, 1418, 1378, 1364, 1234, 1189, 1098, 1028, 1002, 951, 905, 822, 770, 736, 691, 640, 600, 525, 497. MS-ESI: m/z = 328 [M+NH$_4$]$^+$. HRMS-ESI (m/z): [M+Na]$^+$ calcd 333.1825; found 333.1830.

3-bromo-2'-((3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4d).

The title compound was obtained in 28% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.00 (dd, 1H, $J$=2.4Hz, $J$=10.0Hz), 6.60 (d, 1H, $J$=2.4Hz), 6.04 (d, 1H, $J$=10.0Hz), 5.52-5.54 (m, 1H), 3.97 (s, 2H), 3.28 (s, 3H), 2.86-2.90 (m, 2H), 2.22-2.39 (m, 2H), 1.38-1.54 (m, 4H), 1.19-1.26 (m, 2H), 1.11 (s, 3H), 1.04 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.8, 144.8, 144.7, 140.7, 128.2, 116.0, 114.5, 85.3, 77.7, 60.7, 59.8, 57.2, 44.3, 40.1, 36.8, 36.2, 29.9, 29.5, 28.9, 28.7, 21.2. IR[$\nu_{\text{max}}$ cm$^{-1}$] 3314, 3052, 2925, 2852, 2368, 2234, 1719, 1665, 1617, 1563, 1509, 1463, 1415, 1380, 1363, 1329, 1272, 1223, 1189, 1152, 1098, 1028, 1003, 946, 905, 848, 822, 795, 736, 706, 647, 600, 559, 505. MS-ESI: m/z = 411 [M+Na]$^+$. HRMS-ESI (m/z): [M+Na]$^+$ calcd 411.0930; found 411.0934.

3-chloro-2'-((3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4e).

The title compound was obtained in 22% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.90 (dd, 1H, $J$=2.8Hz, $J$=10.0Hz), 6.39 (d, 1H, $J$=2.8Hz), 6.11 (d, 1H, $J$=10.0Hz), 5.52-5.54 (m, 1H), 3.97 (t, 2H, $J$=1.4Hz), 3.27 (s, 3H), 2.87-2.92 (m, 2H), 2.26-2.34 (m, 2H), 1.38-1.50 (m, 4H), 1.14-1.26 (m, 2H), 1.11 (s, 3H), 1.04 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.1, 144.8, 143.1, 136.3, 128.2, 128.1, 114.5, 85.3, 77.7, 59.8, 59.2, 57.1, 44.5, 40.1, 36.9, 36.2, 29.9, 29.5, 28.9, 28.7, 21.1. IR[$\nu_{\text{max}}$ cm$^{-1}$] 3318, 3052, 2926, 2852, 2725, 2368, 2235, 1720, 1666, 1623, 1569, 1534, 1462, 1393, 1379, 1364, 1330, 1259, 1224, 1189, 1150, 1099, 1052, 1028, 1003, 948, 906, 855, 822, 737, 653, 619, 567, 506. MS-ESI: m/z = 362 [M+NH$_4$]$^+$. HRMS-ESI (m/z):
[M+Na]$^+$ calcld 367.1435; found 367.1440.

**ethyl-2'-(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-6-oxo-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-diene-3-carboxylate (4f).**

The title compound was obtained in 5% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (dd, 1H, $J=2.4$Hz, $J=10.0$Hz), 7.44 (d, 1H, $J=2.0$Hz), 6.19 (d, 1H, $J=10.0$Hz), 5.58-5.59 (m, 1H), 4.32 (q, 2H, $J=7.2$Hz), 3.92 (d, 2H, $J=1.2$Hz), 3.21 (s, 3H), 2.96-3.02 (m, 2H), 2.32-2.37 (m, 2H), 1.42-1.49 (m, 4H), 1.37 (t, 3H, $J=7.2$Hz), 1.19-1.23 (m, 2H), 1.13 (s, 3H), 1.06 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.8, 164.4, 150.2, 144.8, 138.7, 128.8, 127.0, 114.7, 85.2, 77.7, 61.4, 59.8, 57.8, 57.1, 44.4, 40.0, 37.0, 36.3, 29.9, 29.5, 29.3, 28.7, 21.3, 14.3. IR[ν$_{max}$ cm$^{-1}$] 3317, 3053, 2926, 2853, 2726, 2593, 2375, 1720, 1666, 1638, 1611, 1579, 1545, 1461, 1412, 1366, 1276, 1254, 1225, 1191, 1098, 1063, 953, 906, 867, 825, 769, 735, 705, 645, 608, 550, 498. MS-ESI: m/z = 405 [M+Na]$^+$. HRMS-ESI (m/z): [M+Na]$^+$ calcd 405.2036; found 405.2041.

**2'-(hept-1-yn-1-yl)-3,4-dimethoxy-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4g).**

The title compound was obtained in 53% yield as a white solid. m.p. 85-87°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.56 (s, 1H), 5.50-5.51 (m, 1H), 5.23 (s, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.91-2.94 (m, 1H), 2.80-2.85 (m, 1H), 2.16-2.34 (m, 2H), 1.97-2.01 (m, 2H), 1.51-1.55 (m, 1H), 1.30-1.43 (m, 5H), 1.14-1.25 (m, 6H), 1.05 (s, 3H), 0.87 (t, 3H, $J=6.8$Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.7, 166.4, 148.4, 145.4, 114.5, 107.7, 102.6, 81.6, 79.5, 56.3, 55.9, 55.5, 43.3, 40.3, 36.8, 36.1, 30.8, 30.5, 29.5, 28.9, 28.8, 28.6, 22.1, 21.2, 18.6, 13.9. IR[ν$_{max}$ cm$^{-1}$] 3255, 3162, 2928, 2860, 2726, 2664, 2377, 2236, 2099, 1871, 1635, 1586, 1454, 1404, 1349, 1319, 1251, 1232, 1189, 1174, 1139, 1071, 1044, 1002, 949, 916, 836, 798, 733, 684, 648, 538, 514, 495, 460. MS-ESI: m/z = 397 [M+H]$^+$ HRMS-ESI (m/z): [M+Na]$^+$ calcd 419.2557; found 419.2560. HPLC on Daicel Chiralpak AS-H, Hexanes / IPA = 90 / 10, 1.0 mL/min$^{-1}$, λ = 220 nm, t (minor 1) = 4.919 min, t (major 1) = 5.714 min, t (minor 2) = 7.280 min, t (major 2) = 8.030 min.

**2'-(hept-1-yn-1-yl)-3-methoxy-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4h).**

The title compound was obtained in 42% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.81 (dd, 1H, $J=3.2$Hz, $J=10.0$Hz), 6.06 (d, 1H, $J=10.0$Hz), 5.50-5.51 (m, 1H), 5.15 (d, 1H, $J=2.8$Hz), 3.66 (s, 3H), 2.87-2.90 (m, 1H), 2.75-2.79 (m, 1H), 2.21-2.27 (m, 2H), 1.97-2.01
2'-((cyclopropylethynyl)-3-methoxy-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-
spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4i).

The title compound was obtained in 32% yield as a light yellow solid. m.p. 86-88°C. 1H NMR (400 MHz, CDCl₃) δ 6.81 (dd, 1H, J=3.2Hz, J=10.0Hz), 6.05 (d, 1H, J=10.0Hz), 5.48-5.50 (m, 1H), 5.12 (d, 1H, J=2.8Hz), 3.66 (s, 3H), 2.88-2.90 (m, 1H), 2.69-2.73 (m, 1H), 2.19-2.25 (m, 2H), 1.46-1.54 (m, 1H), 1.34-1.43 (m, 3H), 1.14-1.21 (m, 2H), 1.10 (s, 3H), 1.00-1.05 (m, 4H), 0.59-0.63 (m, 2H), 0.41-0.45 (m, 2H). 13C NMR (100 MHz, CDCl₃) δ 206.2, 152.4, 145.2, 141.3, 127.8, 114.5, 105.2, 84.7, 74.6, 56.2, 55.1, 44.0, 40.3, 37.4, 36.1, 30.4, 29.5, 28.9, 21.2, 8.2, 8.0, -0.6. IR[νₘₐₓ cm⁻¹] 3401, 3091, 3007, 2927, 2866, 2664, 2370, 2210, 1892, 1736, 1670, 1640, 1587, 1460, 1407, 1364, 1324, 1257, 1235, 1181, 1124, 1039, 978, 901, 828, 797, 748, 690, 622, 545, 490, 448. MS-ESI: m/z = 337 [M+H]+. HRMS-ESI (m/z): [M+H]+ calcd 337.2162; found 337.2165. HPLC on Daicel Chiralpak AS-H, Hexanes / IPA = 90 / 10, 1.0 mL/min⁻¹, λ = 220 nm, t (major 1) = 4.358 min, t (major 2) = 4.945 min, t (minor 1) = 5.980 min, t (minor 2) = 6.505 min.

3-methoxy-5',5'-dimethyl-2'-((phenylethynyl)-3',5',6',7',8',8a'-hexahydro-2'H-
spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4j).

The title compound was obtained in 25% yield as a light yellow liquid. 1H NMR (400 MHz, CDCl₃) δ 7.22 (s, 5H), 6.87 (dd, 1H, J=2.8Hz, J=10.0Hz), 6.12 (d, 1H, J=10.0Hz), 5.55-5.56 (m, 1H), 5.21 (d, 1H, J=2.8Hz), 3.68 (s, 3H), 2.96-3.02 (m, 2H), 2.34-2.40 (m, 2H), 1.40-1.46 (m, 4H), 1.16-1.29 (m, 2H), 1.13 (s, 3H), 1.08 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 206.1, 152.6, 145.5, 141.5, 131.6, 128.1, 127.9, 127.6, 123.6, 114.4, 105.0, 89.4, 81.7, 56.0, 55.2, 44.0, 40.4, 37.9, 36.2, 30.0, 29.5, 28.9, 28.8, 21.2. IR[νₘₐₓ cm⁻¹] 3368, 3053, 2926, 2854, 2725, 2376, 2200, 1952, 1720, 1669, 1639, 1588, 1489, 1460, 1407, 1379, 1236, 1167, 1123, 1035, 974, 913, 828, 798, 757, 692, 631, 536, 489. MS-ESI: m/z = 373 [M+H]+. HRMS-ESI (m/z): [M+H]+ calcd 373.2162; found 373.2162.
373.2168.

3-methoxy-5',5'-dimethyl-2'-(trimethylsilyl)ethynyl)-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (4k).

The title compound was obtained in 23% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.82 (dd, 1H, $J$=2.8Hz, $J$=10.0Hz), 6.07 (d, 1H, $J$=10.0Hz), 5.49-5.51 (m, 1H), 5.13 (d, 1H, $J$=2.8Hz), 3.66 (s, 3H), 2.88-2.91 (m, 1H), 2.75-2.79 (m, 1H), 2.24-2.30 (m, 2H), 1.37-1.54 (m, 4H), 1.13-1.26 (m, 2H), 1.11 (s, 3H), 1.05 (s, 3H), 0.03 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.9, 152.6, 145.3, 141.5, 128.0, 114.2, 106.4, 104.9, 85.7, 56.0, 55.1, 43.9, 40.3, 38.2, 36.2, 30.0, 29.5, 28.9, 21.2, -0.02. IR$[\nu_{\text{max}} \text{ cm}^{-1}]$ 3398, 3051, 2927, 2855, 2663, 2373, 2174, 1946, 1785, 1736, 1671, 1641, 1588, 1460, 1407, 1381, 1323, 1250, 1182, 1123, 1040, 1007, 961, 895, 843, 797, 760, 694, 672, 628, 536, 489. MS-ESI: m/z = 369 [M+H]$^+$.

IR$[\nu_{\text{max}} \text{ cm}^{-1}]$ 3398, 3051, 2927, 2855, 2663, 2373, 2174, 1946, 1785, 1736, 1671, 1641, 1588, 1460, 1407, 1381, 1323, 1250, 1182, 1123, 1040, 1007, 961, 895, 843, 797, 760, 694, 672, 628, 536, 489. MS-ESI: m/z = 369 [M+H]$^+$.

4-methoxy-11-(3-methoxyprop-1-yn-1-yl)-8,9-dimethylspiro[5.5]undeca-2,4,8-trien-1-one (4l-1).

The title compound was obtained in 43% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.86 (dd, 1H, $J$=2.8Hz, $J$=10.0Hz), 6.11 (d, 1H, $J$=10.0Hz), 5.25 (d, 1H, $J$=2.8Hz), 3.95 (t, 2H, $J$=1.8Hz), 3.63 (s, 3H), 3.24 (s, 3H), 3.00-3.06 (m, 1H), 2.53-2.57 (m, 1H), 2.24-2.27 (m, 2H), 1.76 (d, 1H, $J$=16Hz), 1.68 (s, 3H), 1.62 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.5, 151.8, 141.6, 127.6, 123.2, 123.0, 105.6, 86.6, 76.9, 59.8, 56.9, 55.0, 51.3, 42.3, 35.5, 35.3, 18.9, 18.5. IR$[\nu_{\text{max}} \text{ cm}^{-1}]$ 3331, 3050, 2909, 2840, 2733, 2230, 1990, 1720, 1669, 1641, 1587, 1449, 1406, 1356, 1313, 1261, 1237, 1210, 1186, 1147, 1096, 1022, 948, 907, 872, 828, 769, 737, 673, 627, 581, 540, 484. MS-ESI: m/z = 304 [M+NH$_4$]$^+$.

HRMS-ESI (m/z): [M+Na]$^+$ calcd 309.1461; found 309.1467.

4-methoxy-11-(3-methoxyprop-1-yn-1-yl)-8,9-dimethylspiro[5.5]undeca-2,4,8-trien-1-one (4l-1).

The title compound was obtained in 43% yield as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.02 (d, 1H, $J$=2.4Hz), 6.73-6.79 (m, 2H), 5.12 (s, 1H), 4.89 (t, 1H, $J$=1.4Hz), 4.14 (d, 2H, $J$=2.0Hz), 3.90-3.94 (m, 1H), 3.77 (s, 3H), 3.39 (s, 3H), 2.20 (dd, 1H, $J$=5.6Hz, $J$=13.6Hz), 2.05 (dd, 1H, $J$=11.2Hz, $J$=13.6Hz), 1.86 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.3, 148.4, 146.8, 121.0, 118.0, 114.7, 113.2, 110.5, 87.5, 77.6, 77.5, 60.1, 57.5, 55.7, 37.5, 26.0, 22.9, 18.8. IR$[\nu_{\text{max}} \text{ cm}^{-1}]$ 3438, 3092, 2932, 2835, 2375, 2058, 1690, 1646, 1617, 1588, 1490, 1431, 1375, 1281, 1226, 1087, 1039, 964, 906, 817, 736, 704, 561, 491. MS-ESI: m/z = 304 [M+NH$_4$]$^+$.
HRMS-ESI (m/z): [M+Na]⁺ calcd 309.1461; found 309.1469.

4-methoxy-11-(3-methoxyprop-1-yn-1-yl)-8-methylspiro[5.5]undeca-2,4,8-trien-1-one (4m-1).
The title compound was obtained in 30% yield as a light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 6.86 (dd, 1H, J=3.2Hz, J=10.0Hz), 6.11 (d, 1H, J=10.4Hz), 5.40-5.41 (m, 1H), 5.28 (d, 1H, J=3.2Hz), 3.95 (t, 2H, J=1.6Hz), 3.63 (s, 3H), 3.24 (s, 3H), 3.06-3.10 (m, 1H), 2.51-2.56 (m, 1H), 2.16-2.32 (m, 2H), 1.90 (dd, 1H, J=5.6Hz, J=17.2Hz), 1.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 204.7, 151.8, 141.6, 131.5, 127.6, 118.4, 105.4, 86.5, 77.2, 59.8, 57.0, 55.0, 50.3, 36.5, 35.4, 33.9, 22.9. IR[νmax cm⁻¹] 3332, 2926, 2851, 2731, 2372, 2230, 1980, 1721, 1668, 1642, 1587, 1449, 1407, 1358, 1322, 1258, 1235, 1208, 1186, 1137, 1098, 1026, 1003, 946, 912, 856, 829, 792, 768, 671, 560, 535, 489, 440. MS-ESI: m/z = 290 [M+NH₄⁺]. HRMS-ESI (m/z): [M+Na]⁺ calcd 295.1305; found 295.1311.

6-methoxy-4-(3-methoxyprop-1-yn-1-yl)-2-methyl-2-vinylchromane (4m-2).
The title compound was obtained in 35% yield as a light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.01 (s, 1H), 6.73-6.79 (m, 2H), 6.03 (dd, 1H, J=10.8Hz, J=17.6Hz), 5.33 (d, 1H, J=17.2Hz), 5.12 (d, 1H, J=11.2Hz), 4.13 (s, 2H), 3.91-3.95 (m, 1H), 3.77 (s, 3H), 3.38 (s, 3H), 2.15 (dd, 1H, J=6.0Hz, J=13.6Hz), 2.01 (dd, 1H, J=10.8Hz, J=13.6Hz), 1.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 146.6, 142.5, 120.9, 118.1, 114.7, 113.4, 113.1, 87.6, 77.5, 75.5, 60.1, 57.4, 55.7, 38.5, 25.9, 23.4. IR[νmax cm⁻¹] 3417, 3088, 2930, 2836, 2596, 2378, 2237, 2060, 1854, 1736, 1689, 1618, 1489, 1431, 1375, 1284, 1221, 1096, 1038, 990, 929, 868, 818, 734, 705, 680, 555, 512. MS-ESI: m/z = 290 [M+NH₄⁺]. HRMS-ESI (m/z): [M+Na]⁺ calcd 295.1305; found 295.1305.

4-methoxy-8-methyl-11-(phenylethynyl)spiro[5.5]undeca-2,4,8-trien-1-one (4n-1). The title compound was obtained in 23% yield as a light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.23(s, 5H), 6.91 (dd, 1H, J=2.8Hz, J=10.0Hz), 6.16 (d, 1H, J=10.0Hz), 5.43-5.44 (m, 1H), 5.33 (d, 1H, J=2.8Hz), 3.65 (s, 3H), 3.20 (dd, 1H, J=6.0Hz, J=11.6Hz), 2.60-2.65 (m, 1H), 2.24-2.40 (m, 2H), 1.94 (dd, 1H, J=5.2Hz, J=17.2Hz), 1.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 204.9, 151.9, 141.6, 131.5, 131.4, 128.0, 127.8, 127.6, 123.4, 118.4, 105.4, 89.4, 81.7, 55.0, 50.5, 36.3, 36.0, 33.9, 23.0. IR[νmax cm⁻¹] 3330, 3059, 2916, 2849, 2372, 2346, 2200, 1949, 1878, 1852, 1774, 1738, 1687, 1666, 1639, 1589, 1562, 1544, 1509, 1460, 1407, 1375, 1232, 1207, 1174, 1104, 1031, 854, 825, 789, 758, 724, 692, 535, 488.
MS-ESI: m/z = 305 [M+H]^+. HRMS-ESI (m/z): [M+H]^+ calcd 305.1536; found 305.1532.

**6-methoxy-2-methyl-4-(phenylethynyl)-2-vinylchromane (4n-2).**

The title compound was obtained in 44% yield as a light yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.43 (m, 2H), 7.28-7.30 (m, 3H), 7.10 (d, 1H, J=2.4Hz), 6.75-6.84 (m, 2H), 6.06 (dd, 1H, J=10.8Hz, J=17.2Hz), 5.36 (dd, 1H, J=0.8Hz, J=17.2Hz), 5.15 (dd, 1H, J=0.8Hz, J=10.8Hz), 4.10 (dd, 1H, J=6.0Hz, J=10.4Hz), 3.77 (s, 3H), 2.22 (dd, 1H, J=6.0Hz, J=13.6Hz), 2.11 (dd, 1H, J=10.4Hz, J=13.6Hz), 1.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.3, 146.6, 142.5, 131.6, 128.2, 127.9, 123.3, 121.1, 118.1, 114.7, 113.4, 113.2, 90.5, 82.0, 75.6, 55.7, 38.4, 26.4, 23.5. IR[νmax cm⁻¹] 3059, 2929, 2855, 2375, 2226, 2066, 1954, 1878, 1689, 1598, 1492, 1427, 1373, 1266, 1219, 1146, 1093, 1039, 927, 911, 812, 757, 692, 531, 485. MS-ESI: m/z = 305 [M+H]^+. HRMS-ESI (m/z): [M+H]^+ calcd 305.1536; found 305.1529.
$^1$H and $^{13}$C NMR Spectra of Compound 5a
$^1$H and $^{13}$C NMR Spectra of Compound 4a

X-ray Analysis of Compound 4a.
The crystallographic data of 4a were summarized in the following table.

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CIF file of 4a can be obtained from the Cambridge Crystallographic Data Centre using deposition number CCDC 1447716. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:+44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk].
$^1$H and $^{13}$C NMR Spectra of Compound 4b
$^1$H and $^{13}$C NMR Spectra of Compound 4c
$^1$H and $^{13}$C NMR Spectra of Compound 4d
1H and 13C NMR Spectra of Compound 4e
$^1$H and $^{13}$C NMR Spectra of Compound 4f
$^1$H and $^{13}$C NMR Spectra of Compound 4g
HPLC Spectra of Compound 4g

![HPLC Spectra](image)

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$^1$H and $^{13}$C NMR Spectra of Compound 4h
$^1$H and $^{13}$C NMR Spectra of Compound 4i
HPLC Spectra of Compound 4i
$^{1}$H and $^{13}$C NMR Spectra of Compound 4j
$^1$H and $^{13}$C NMR Spectra of Compound 4k
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